# DETERMINATION OF HEAVY METAL CONCENTRATION IN SURFACE AND SUB SURFACE SOIL AROUND ULU TUALANG NEWLY-CLOSED LANDFILL, TEMERLOH, PAHANG

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# ABSTRACT

European community had been stated 13 types of heavy metals that have the highest concern. There were including As, Cd, Co, Cr, Cu, Hg, Mn, Ni, Pb, Sn, and Tl. Some of these heavy metals such as Cu and Ni are actually necessary to our human body but mostly are very dangerous to our health for example Cu can cause cardiovascular disease while can cause cytotoxic role in plant if in excessive amount. This heavy metal pollution in soil is usually occurring in landfill that near the industrial estate. This situation become worst when there is no proper dumping system in that particular area. So, this research will be conducted to determine the presence and distribution of copper and nickel in surface and sub-surface soils around Ulu Tualang Newly-Closed Landfill, Temerloh, Pahang. This research data will become reference for the landfill management and reconstruction. Samples obtained by digging at different point and two samples for each point, one for surface and one for sub-surface soil. The sample heated using oven, pulverized and sieve to get homogeneity. After that the sample digested using SCL (South California Laboratory) method that used HCl and $HNO_3$ as the digester. After dilution and vacuum filtered the sample analyzed using Atomic Absorption Spectrophotometry (AAS). For the result, after the sample spiked Cu was detected at 19.2-70.35 mg/kg while Ni was detected around 51.25-99.65 mg/kg. As a conclusion, for the depth differences, the distribution of the heavy metal seems did not have pattern and Ni concentration are higher than copper for both soil layers.

# ABSTRAK

Masyarakat Eropah telah menyatakan 13 jenis logam berat yang memiliki kepedulian yang tertinggi. Ini termasuklah As, Cd, Co, Cr, Cu, Hg, Mn, Ni, Pb, Sn, dan Tl. Beberapa logam berat seperti Cu dan Ni sebernarnya diperlukan untuk tubuh manusia kita tetapi sebahagian besar sangat berbahaya untuk kesihatan kita misalnya Cu boleh menyebabkan penyakit jantung sementara boleh menyebabkan peranan sitotoksik dalam tanaman jika dalam jumlah berlebihan. Pencemaran logam berat dalam tanah biasanya terjadi pada tapak pelupusan yang berdekatan dengan kawasan industri. Situasi ini menjadi lebih buruk apabila tidak ada sistem pelupusan yang sewajarnya di kawasan tersebut. Oleh itu, kajian ini akan dilakukan untuk menentukan kewujudan dan taburan tembaga dan nikel dalam permukaan tanah dan sub-permukaan sekitar tapak pelupusan Ulu Tualang yang telah ditutup, Temerloh, Pahang. Data kajian ini akan menjadi panduan bagi pengurusan tapak pelupusan dan rekonstruksi. Sampel diperolehi dengan menggali pada titik yang berbeza dan dua sampel untuk setiap titik, yang pertama untuk permukaan dan satu untuk sub-permukaan tanah. Sampel dipanaskan menggunakan ketuhar, dihaluskan dan ditapis untuk mendapatkan aduan sempurna. Setelah itu sampel dicerna menggunakan kaedah SCL (South California Laboratory) yang mengunakan HCL dan $HNO_3$ sebagai pencerna. Setelah dicairkan dan ditapis, sampel dianalisis menggunakan Spektrofotometri Serapan Atom (SSA). Keputusannya, Cu dikesan pada 19.2-70.35 mg/kg sedangkan Ni dikesan sekitar 51.25-99.65 mg/kg. Sebagai kesimpulan, atas perbezaan kedalaman, taburan logam berat nampaknya tidak mempunyai pola dan kepekatan nikel lebih tinggi dari tembaga untuk kedua-dua lapisan tanah.

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# LIST OF ABBREVIATION

| | | |
|---|---|---|
| Ni | - | Nickel |
| Cu | - | Copper |
| US EPA | - | United State Environmental Protection Agency |
| SCL | - | Southern California Labratory |
| ASTM | - | American Society Of Testing And Materials |
| MSW | - | Municipal Solid Waste |
| GCL | - | Geomembrane Clay Liner |
| PVC | - | Polyvinyl Chloride |
| CPE | - | Chlorinated Polyethylene |
| CSPE | - | Chlorosulphonated Polyethylene |
| EPDM | - | Ethylene Propylene Rubber |
| PP | - | Polypropylene |
| LLDPE | - | Linear Low-Density Polyethylene |
| MDPE | - | Medium-Density Polyethylene |
| HDPE | - | High- Density Polyethylene |
| $CH_4$ | - | Methane |
| $CO_2$ | - | Carbon Dioxide |
| $HNO_3$ | - | Nitric Acid |
| $H_2O_2$ | - | Hydrogen Peroxide |
| AAS | - | Atomic Absorption Spectroscopy |
| XRF | - | X-Ray Fluorescence Radioisotope |
| Ca | - | Calcium |

| | | |
|---|---|---|
| EDTA | - | Ethylene-Diamine-Tetra-Acetic |
| $NO_2$ | - | Nitrogen Dioxide |
| FLAA | - | Flame Atomic Absorption Spectrometry |
| GFAA | - | Graphite Furnace Atomic Absorption |
| ICP-AES | - | Inductively Coupled Plasma Atomic Emission Spectrometry |
| ICP-MS | - | Inductively Coupled Plasma Atomic Emission Spectrometry |
| ppm | - | Part Per Million |
| Df | - | Dilution Factor |
| HCl | - | Hydrochloric Acid |
| PEL | - | Permissible Exposure Limit |

# CHAPTER 1

# INTRODUCTION

## 1.1 Research background

As we know Malaysia is a country that has a high industrial technology in manufacturing and production process. Therefore, this country is very dependent in using a large amount of metals especially in construction site; processing plant and mining industry. All of these activities are producing massive amount of waste than contain very high concentration of heavy metal. These heavy metal wastes are usually thrown away by some industrial companies to the landfill area without treating them. In a couple of years, the concentration of these heavy metals will increase rapidly and will start to affect the surrounding area. This heavy metal pollution did not just stop bring harms to human, but also to animal, plant and the ecosystem.

## 1.2 Problem statement

Most of people did not concern about heavy metal pollution especially at the landfill. They just think a landfill is an area that used for dispose their factory and domestic waste. Most landfill sites are open dump without a proper leachate or gas collecting and treating system (Roongtanakiat *et al.,* 2003). An unlined landfill cannot prevent leacheate flowing to the area around the landfill sites and underground water beneath it. The leacheate are usually containing high concentration of heavy metal (Roongtanakiat *et al.,* 2003).

When the heavy metal contaminated the water bodies and the water used by human or animal, they will suffer serious damages to their vital organ due to the toxicity (Yadav, 2009). While the land that contaminated with this heavy metal cannot be use for plantation or farming because the soil will have very high acidity level. So the purpose of this study is to determine the heavy metal concentration at Ulu Tualang closed landfill in order to make sure the level of the heavy metal concentration is in safe condition.

## 1.3 Objectives

i. To determine the presence and distribution of heavy metals (Ni and Cu) concentration in soil taken from the newly-closed Ulu Tualang landfill.

ii. To determine the differences of heavy metal concentration between surface and sub-surface soil.

## 1.4 Scope of Research

### 1.4.1 Type of Heavy Metal

In this study, there are two types of metal that will be focus. The first one is nickel and the second one is copper. Nickel is a silvery-white lustrous metal, belongs to transition metal element category and has a high melting point (1453°C). It is hard, ductile and can be used for anti-corrosion purpose due to its properties. Nickel and its compound are mainly used in construction, automobile manufacturing and battery production.

Copper is a transition metal that belongs to Group 11 of the periodic table. Its melting point is around 1084°C and has a good thermal conductivity around 401

$W.m^{-1}.K^{-1}$. Copper are usually used as electrical conductor and become important material in building construction. Cu concentration in landfill is quite high when clothing and wood industries waste founded while high Ni values might be contributed to metal processing or municipal waste including batteries (Kasassi *et al.*, 2007).

### 1.4.2 Area Description & Layer of Soil

There are 5 layers in soil structure including O-horizon (0-2 inch), A-horizon (2-10 inch), B-horizon (10-30 inch), C-horizon (30-48 inch) and R-horizon. In this research, the heavy metal concentration analysis will conducted only for A and B-horizon layer. Surface soil (A-horizon) is the layer that below the O-horizon layer and contain a lot of organic matter. Sub-Soil (B-horizon) is a zone of accumulation to occur and consist of mineral layers.

The Ulu Tualang closed landfill is located at Mukim Mentkab, Temerloh, Pahang state of Malaysia. The landfill is near the Temerloh Industrial Estate and Mentakab Industrial Park that focusing in stainless steel fabrication and wood base industry. As additional information, there are 15 landfills are located in Pahang state. 13 of them are operated by Alam Flora including the Ulu Tualang Landfill. The landfill had been closed in 30th June 2010 and handed over to Cypark Resource Sdn. Bhd.

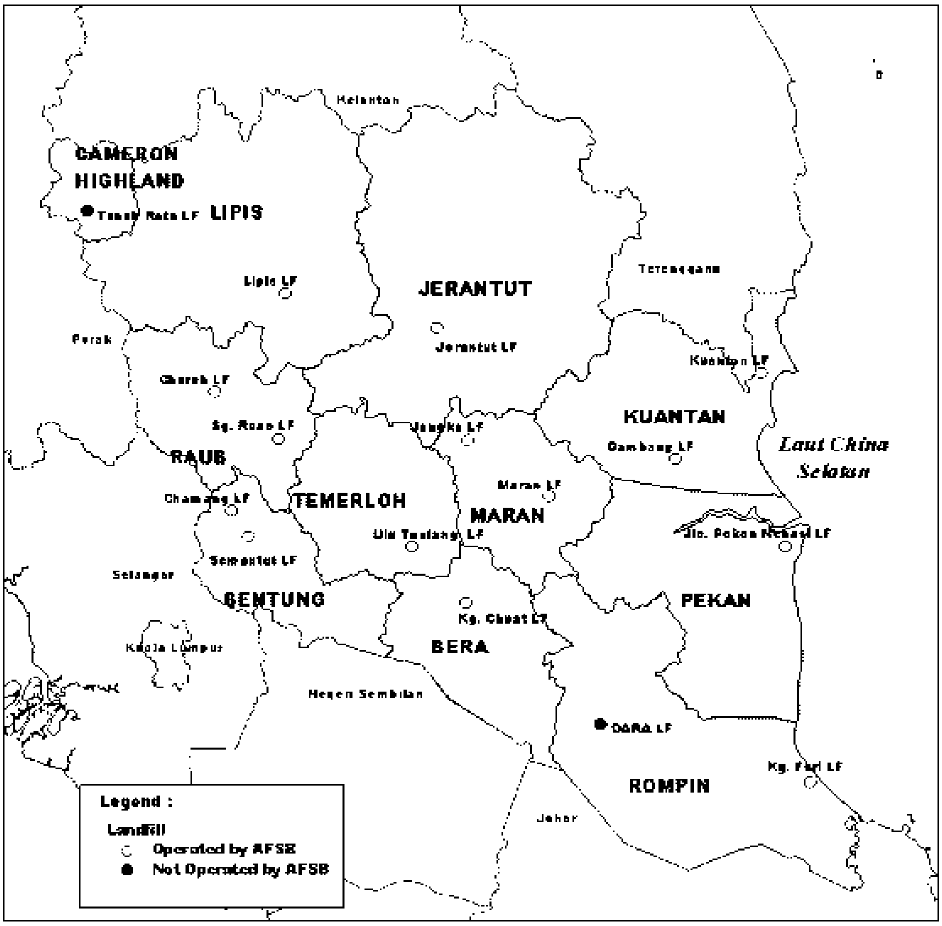


**Figure 1.1** Location map of Ulu Tualang closed landfill

The company list that probably using the landfill ;

i. Megaply Industries (M) Sdn Bhd (Plywood & Veneers).
ii. Intan Suria Sdn Bhd (Frames - Picture,Wood Products).
iii. SQ Wooden Picture Frame Moulding Sdn Bhd (Picture Frames - Wholesaler & Manufacturers).
iv. LCS Precast Sdn Bhd (Piling).
v. Mentakab Stainless Steel Works (Stainless Steel Fabricators).
vi. Syarikat Perniagaan Boon Wee (Biscuits - Wholesaler & Manufacturers,Food Products).
vii. Mentakab Agricultural Machinery Sdn Bhd (Agricultural Equipment & Supplies, Tractor Distributors & Manufacturers).

### 1.4.3 Acid Digestion Method

There are several types of acid digestion method that can be used for heavy metal extraction such as US EPA (Eniromental Protection Agency) method 3050, SCL (Southern California Labratory) method, ASTM (American Society of Testing and Materials) method and US EPA method 6020. For this research, the method that will focused is the SCL method. The detail methodolgy will be explained at the next chapter.

## 1.5 Rational and Significance

The purpose of this experimental research conducted is to get the mean value of copper and nickel concentration in Ulu Tualang newly-closed landfill. With this mean value, it can be compared to US EPA soil standard to make sure either the area have in the safe level. Besides that, statistical data that obtained will be very useful for this landfills management for treatment and soil remediation purpose.

# CHAPTER 2

# LITERATURE REVIEW

## 2.1 Overview

This chapter wills reviews the types of landfills such as landfill for commingled MSW, landfill for shredded solid waste and monofills landfills. It also will review the element of landfill closure plan, part of sanitary landfill, Ni and Cu toxicology, an overview of sampling processing and analysis, Ni and Cu alternative removal and a brief of in-situ measurement. Besides that, a previous research also will be reviewed.

## 2.2 Types of Landfills

### 2.2.1 Landfills for Commingled MSW

Municipal solid waste (MSW) usually comes from household waste and industrial waste. So major of the landfills in this world are designated for commingled MSW. This type of landfill also accept limited amount of nonhazardous industrial wastes and sludge wastewater treatment plants. Demand for this type of landfill is very high even abandoned or closed landfills in some locations are being reused by excavating the composed material and some cases, the composed material stockpiled, and a liner is installed before the landfill is reactivated for landfilling purpose (Tchobanoglous *et. al*., 1993).

### 2.2.2 Landfills for Shredded Solid Waste

This type of landfill is an alternatives ways to solid waste disposal where it involving shredding steps for the solid wastes before places them in a landfill. With this new method, the shredded solid waste can be placed at up to 35 percent greater density than the common method. On the other hand, it also had disadvantages including needs of highly cost shredding facility. But it can save a lot of money in areas where landfill capacity is very expensive and can produce compost that can be used as intermediate cover material (Tchobanoglous *et. al*., 1993).

### 2.2.3 Landfills for Individual Waste Constituents

Known as monofills, these landfills typically accept combustion ash, asbestos, and other similar waste. The designated wastes usually isolated from common solid waste. This type of waste are nonhazardous but may release constituents in concentration that exceed applicable water quality and sometimes contains small amounts of unburned organic material that will causing odors problems. Gas recovery system usually recommended for solving this problems (Tchobanoglous *et. al*., 1993).

## 2.3 Element of Landfill Closure Plan

### 2.3.1 Final Cover Design

For the first element of the closure plan is the final cover design. The surface that placed over a landfill that wanted to be closed called final cover. It is very important to design this final cover following the parameters to make sure it can functional to control the emissions of the landfill and can support the growth of vegetation process. Vegetation is the favorite method that used for covering the closed landfill site. So, when planning the landfill closure, the planners should select the best plant that can survive for this purpose. Besides that, the planner also must plan the type, density, permeability and thickness of soil that will be used for covering the landfill (Tchobanoglous *et. al*., 1993).

### 2.3.2 Surface Water Control Design

The second element is the drainage control design. Drainage control system is very important to prevent and controlling the surface water from penetrate the final cover. The worst case scenario of a landfill is when the surface water penetrates the cover soil and leach the heavy metal to the underground water. There are several features that should be consider when design the drainage control system including (Tchobanoglous *et. al*., 1993);

1. The shortest distance of collecting and routing of surface water off from the landfill.
2. Selection of channel and drainage ways
3. Calculating the slope to maximize the removal of surface water.
4. Specification of material that used for the drainage for easier maintenance.

### 2.3.3 Landfill Gases Control Design

The third element is the landfill gases control design. A landfill gas control system is very important for an active landfill or a closed landfill. This is important because, gases such as methane are continuously generated from the landfill. The crucial steps for designing a gas control system are selection of material and the placement of wellheads, valves, and collection pipes in the final cover. The material should be flexible and strong enough for various conditions. It is also important to consider the quantity of methane gas production for combustion process (Tchobanoglous *et. al*., 1993).

### 2.3.4 Leachate Treatment & Control Design

The forth element is the leachate treatment and control design. Besides contaminating the sub surface soil, leachate also can mobilize the contaminant further to the underground water. To minimize the problem, the planner should reconsider the final cover design, the types of waste placed in the landfill, the climate and precipitation of the area (Tchobanoglous *et. al*., 1993). Some of modern countries start using green technology to control the leachate such as using Vitever grass to absorb the leachate content in the soil (Roongtanakiat *et. al*., 2003).

### 2.3.5 Environmental Monitoring Facilities Design

The final part of the plan is designing the environmental monitoring facilities. These facilities are very important to make sure that the integrity of the landfill is maintained. The plan usually follows the guidelines of the regulatory agency. Monitoring facilities that usually installed are groundwater monitoring wells, vadose zone lysimeters, gas vents, leachate treatment facilities and storm water holding basins (Tchobanoglous *et. al*., 1993).

## 2.4 Part of Sanitary Landfill

### 2.4.1 Bottom Liner System

Function of a bottom liner is to prevent the trash from coming in contact with the outside soil, particularly the groundwater**.** There 3 types of liner that usually used such as clay liner, plastic liner and composite liner. Geomembrane clay liner or GCLs are comprised of a thin layer of sodium or calcium bentonite bonded to a layer or layers of geosynthetic (Bouazza,2001). The geosynthetics are either geotextiles or a geomembrane.

For plastic liner, the liner are from synthetic material such as polyvinyl chloride (PVC), chlorinated polyethylene (CPE), chlorosulphonated polyethylene (CSPE), ethylene propylene rubber (EPDM), polypropylene (PP), linear low-density polyethylene (LLDPE), medium-density polyethylene (MDPE) and, more recently, the bituminous geomembrane. A research by Rowe and Sangam (2002) stated that High- density polyethylene (HDPE) geomembranes have been used exclusively in landfill applications, especially for bottom liners, because of their relatively high resistance. While a composite liner is a liner of two component, a geomembrane and a layer of permeability soil (Giroud and Bonarpate, 1989).

### 2.4.2 Water Drainage and Leachate Collecting System

The purpose of a leachate collection and removal system is to remove contaminated water from the base of a landfill waste containment cell for the purpose of minimizing the hydraulic head on the liner system or subgrade of the landfill cell (Warith *et. al*., 2004). A leachate collection and removal system should consist of a granular soil layer or geocomposite drainage layer of adequate long-term hydraulic conductivity so as to collect the leachate being transmitted through the waste mass (Koerner and Soong, 2000).

### 2.4.3 Methane Collection System

When solid waste is buried in a landfill, the biodegradable fractions of the solid waste will be decompose via a complex series of microbial and abiotic reactions. Methane ($CH_4$), one of the terminal products, is formed by methanogenic microorganisms under anoxic conditions, either through the direct cleavage of acetate into $CH_4$ and carbon dioxide ($CO_2$) or the reduction of $CO_2$ with hydrogen (Spokas *et. al*., 2006).

Methane that produce from the landfill can be used to fuel industrial or commercial boilers, to generate electricity using internal combustion engines or gas turbines, and to produce a substitute natural gas suitable for compression or pipeline transport. Beside supplying the energy, recovery of methane from the landfill also can reduce global warming because methane is second most important greenhouse gas.

## 2.5 Heavy Metal Toxicology

### 2.5.1 Copper Toxicology

Copper plays important role in ecosystem including $CO_2$ assimilation, ATP synthesis and considered as a micronutrient for plants (Yadav, 2009). On the other hand, when it in excess amount, it can bring harms to human, animal and plant. The increasing of Cu can be enhancing by many factors. There are including industrial and mining activities. High concentration of Cu in soil can plays cytotoxic role, induces stress and cause injury to plant that leads to plant retardation and leaf chlorosis (Lewis *et al.*, 2001). For human, excess amount of Cu can cause cardiovascular disease and diabetes while acute Cu toxicity can result in liver disease and neurological defects (Uriu-Adams and Keen, 2005).

### 2.5.2 Nickel Toxicology

Nickel is also can bring many negatives effects to our health and the ecosystem if in excessive amount. Similar with the Cu, the Ni level in soil can be enhancing by mining activity, industrial waste and open burning of coal. Plant grown in high Ni containing soil showed impairment of nutrient of nutrient balance and resulted in disorder of cell membrane functions (Yadav, 2009). Human that lives in that polluted area will have percentage to get lung cancer due to its carcinogenic properties (Kasprzak *et al*., 2003).

## 2.6 Sample Processing & Analysis

To determine the concentration of the heavy metal compound in the landfill soil, a suitable method must be chosen in order to get the accurate value. There were several method had been used by other researchers to processing the sample. The first step is the sample collecting. The common method is using a driller. Drilling depth sometimes had to be extending to find the maternal rock and to get a varied depth of the wells (2.3-17.5m) because the thickness of waste in the landfill is varied (Kasassi *et al.,* 2007). The sampling point can be chosen randomly or systematically using gridding method.

For the second step is sample digestion. The sample that obtained from the first step must be digesting to extract the heavy metal compound from the soil. The best method needed to make sure the heavy metal is fully extracted and give the real concentration level when conduct the analysis stage. For pollutant inputs are not silicate-bound, a 'pseudo total' analysis of strong acid digest such as aqua-regia digestion method is sufficient (Sabienë *et al.*, 2004). The alternative way is digesting the sample with $HNO_3$ and $H_2O_2$ using the Method 3050B suggested by USEPA (Chen *et al.,* 2004).

Besides using chromatographic separation and spectroscopic techniques such as Atomic Absorption Spectroscopy (AAS), in situ analysis method can be used to reduce time and effort that needed to extract the sample before can analysis it. The capability to perform direct, in situ analysis of solid soil sample, without the need for digestion as is potentially available through portable XRF instruments would be a major step forward (Radu and Diamond, 2008). A fast method for sure gives a lot of advantages especially when it comes to human health issues. This will be discussing further in the next subtopic.

## 2.7 Ni and Cu Alternative Removal Techniques

Different from Method 3050B and aqua-regia digestion method, removing copper, Cu from contaminated landfill soil using flushing method is quite challenging. Flushing Cu from the soil with 0.1M aqueous solution of ethylene-diamine-tetra-acetic (EDTA) reported can be maximize the extraction efficiency about 60% (Palma and Medici, 2002) can give a reason why this study still get a place for further research. Beside ex-situ method, in-situ removal techniques are a very important due to its potential to become the main rapid treating method for heavy metal pollution. One of the most popular is the electro-kinetic removal technique. It relies on the application of low-density direct current between electrode placed in the soil and works due to the presence of enough moisture in the soil particle to have an inherent electrical conductivity (Ravera *et al.,* 2005).

On the other side, nickel removal from soil also becomes the main title for many researches. As a fact, not all of the heavy metal can be easily flush from the soil including Ni and Cu. Therefore, most of this intellectual person starts to think to prevent the metals to transport into the soil (Imperato *et. al.*, 2003). And the result, the come with a solution that is using calcium (Ca) as the factor to increase the Ni desorption level into the soil. Ca can compete strongly with other metals to get adsorption sites on the mineral surface (Wang *et al*., 1996) and automatically can prevent other hazardous metal to pollute the soil. As we know, Ca is a not hazardous element even taken in a high concentration.